12/2/75

EEE BRANCH REVIEW

DATE:	IN ____ OUT ____	IN 11/11/75 OUT 12/2/75	IN ____ OUT ____
	FISH & WILDLIFE	ENVIRONMENTAL CHEMISTRY	EFFICACY

FILE OR REG. NO. 464-EUP

PETITION OR EXP. PERMIT NO. ____

DATE DIV. RECEIVED 11-4-75

DATE OF SUBMISSION 10-31-75

DATE SUBMISSION ACCEPTED ____

TYPE PRODUCT(S): I, D, (H) F, N, R, S Brush Control

PRODUCT MGR. NO. SRS

PRODUCT NAME(S) Grazon 3

COMPANY NAME Dow Chemical

SUBMISSION PURPOSE EUP

CHEMICAL & FORMULATION 3,5,6,-trichloro-2-pyridyloxyacetic acid as the triethylamine salt also triclopyr

1.0 Introduction

Applicant proposes an experimental use permit for the herbicide chemical 3,5,6-Trichloro-2-pyridyl-oxyacetic acid for use to control woody plants and broadleaf on rights-of-way, forests and industrial sites.

Product name is Grazon 3.

Common chemical name is triclopyr. Chemical name for the active ingredient is 3,5,6-Trichloro-2-pyridinyloxyacetic acid.

Product is also known as M-3724 and Dowco 233.

The active ingredient is formulated as its triethylamine salt in product Grazon 3.

Product contains 3 lbs active ingredient per gallon.

See previous review (R.W. Cook, 4-5-74) of Dowco 233 [M-3724] submission of 2-25-74.

Applicant proposes total quantity of 6328 gallons or 18,984 pounds of active ingredient.

2.0 Directions for Use

Use 1-3 quarts Grazon 3 to make 100 gallons of spray solution and use 100-400 gallons per acre depending on size and density of brush. Dosage is 0.75 - 9 lbs active ingredient per acre. May be tank mixed with 1-4 quarts of DMA 4, Formula 40, Esteron 99 Concentrate or Tordon 101 Mixture Herbicide.

[Note these tank mixtures differ slightly from previous submission]

Other uses at lower or comparable rates.

Do not apply Grazon 3 directly to, or otherwise permit it to come into direct contact with vegetable crops, flowers or other desirable broadleaf plants. Do not graze treated area or feed treated forage.

3.0 Discussion of Data

Soil Metabolism Study:

Reference D.2.0 D.2.1

"Aerobic Decomposition Rates of ^{14}C-Triclopyr in Several Soils (Status Report)" D. A. Laskowski, H. D. Bidlack, L. B. Comeaux. Report dated October 16, 1975.

Four soils were treated with ^{14}C-triclopyr labeled in the 2 and 6 position of ring. Concentration in soil was 1 ppm ($1 * 10^6$) dpm). Treated soil incubated at three temperatures in soil biometer flasks. Triclopyr extracted from soil by shaking 5-9 grams soil with 10 ml of 0.1 M HCl or 1.5 M H_3PO_4 and 15 ml diethyl ether. Procedure claimed to be quantitative. Aliquots combusted and counted; other aliquots to TLC, then counted.

Soil Characteristics

Code	Source	Series	1/3 Bar	Sand	Silt	Clay	pH	Org. Carbon.
108	Illinois	Flanagan	26.3	14	54	32	5.8	4.2
108-1	Illinois	Flanagan	27.7	20	52	28	5.2	---
106	California	Yolo	21.8	50	34	16	6.5	0.8
110-1	Mississippi	Commerce	22.1	23	52	20	6.6	---

Results

Results are reported as % of parent compound remaining in soil. No material balance of ^{14}C nor identification of other ^{14}C-containing compounds. It is not known whether non-accounted ^{14}C was lost as $^{14}CO_2$; other volatile products, or remainedin the soil or extracts.

Halflife of parent compound at 25°C and 35°C was less than 50 days in 3 soils. Three halflives of parent ranged up 249 days. The fate of non-parent material is unknown.

At 15°C the first half-life in two soils ranged from 79 to 156 days, while three halflives ranged up to 370 days.

% of Applied Triclopyr Remaining

Soil/Days	0	7	14	28	56	90-100	249-255	373
108 @ 35°C	97.2	63.6	33.2	19.3	16.3	12.3	----	----
106 @ 35°C	99.2	88.9	84.4	62.2	40.5	30.9	6.8	----
108-1 @ 25°C	90.5	83.3	28.4	8.8	7.9	2.5	----	----
110-1 @ 25°C	87.3	79.9	66.0	30.1	11.1	---	----	----
108 @ 15°C	97.2	----	78.1	73.2	56.1	40.3	15.3	6.0
106 @ 15°C	99.2	----	93.6	89.3	81.3	71.7	23.3	12.0

Halflives of Parent

Soil	Temp	1st 1/2 life	3 Halflives
108	35	10	90
106	35	46	<249
108	25	8	< 28
110	25	18	< 56
108	15	79	<373
106	15	156	373

Conclusions

The data is adequate for experimental permit. However, for registration, we will need the final report on this study. The final report must include material balance which accounts all ^{14}C including $^{14}CO_2$, volatile organic ^{14}C, and non-extractable ^{14}C. Data on formation and decline of transformation products is needed.

Soil Leaching Study:

Reference D.3.0 D.3.1

"Column Leaching Studies with Triclopyr and Picloram - A Report" Report by R. L. Zimdahl, Colorado State University submitted to Dow Chemical April 14, 1975.

A sandy loam soil (sand 64, silt 20, clay 14, pH 7.5 and 1.6% organic matter) was treated with ^{14}C-triclopyr at unspecified rate. The position of the ^{14}C in the triclopyr molecule is also unspecified. Soil columns were 4 inches or 12 inches long, with the top 1 inch segment being treated soil. Some treated soil aged 30 days prior to placement in soil column. Other soil leached with aging. One column was leached continuously, while another was leached 5 days then allowed to dry 2 days, serially up to 28 days. Similar columns treated with picloram were leached in parallel manner. Each column was treated with 100,000 dpm. Analytical method based on ^{14}C only; parent compound not accounted specifically.

Results

Average material balance in the five soil columns was 50.2% of ^{14}C applied. Of the ^{14}C applied 37.3% was eluted through columns and 12.9% was retained in soil. However, of the accountable ^{14}C, 74% leached through and 26% was retained in soil. Applicant provides no explanation of the low accountability. In parallel soil columns using picloram, material balance was 97.9% with 86.9% eluted and 11.0% retained in soil.

There appears to be little difference between elution patterns of 4 inch columns compared to 12 inch columns. Study provides no information on the identity of leached or non-leached ^{14}C or whether ^{14}C is bound to soil since soil samples combusted without any extraction procedure.

No	Column Length	Pretreatment	CPM Eluate (%)	CPM Soil	CPM Total
1	4	None	34739 (34.7)	4558 (4.5)	39297 (39.3)
2	12	None	31148 (31.1)	26816 (26.8)	57964 (57.9)
3	12	Aged 30 days	40982 (40.9)	13262 (13.3)	54244 (54.2)
4	4	Continuous Leach	40362 (40.3)	13635 (13.6)	53997 (54.0)
5	4	Intermittent Leach	39630 (39.6)	6338 (6.3)	45968 (46.0)
		Average	37372 (37.3)	12921 (12.9)	50294 (50.3)

Conclusions

Triclopyr is a leacher, but the chemical nature of leached ^{14}C is not known.

Soil Field Leaching Study

Reference D.3.0 D.3.1

"Column Leaching Studies with Triclopyr and Picloram - A Report" Report by R.L. Zimdahl, Colorado State University submitted to Dow Chemical April 14, 1975.

Triclopyr at rates of 0.5, 3, and 9 lbs ai/A was used to treat field soil contained in 6-inch steel cans which had been driven into soil. Experimental design precluded study of leaching and rate or mode of degradation. Measurement of persistence of phytotoxicity to cucumbers was performed by bioassay. Field soil was treated on unspecified date and at unspecified intervals later, sunken cans were planted to cucumbers. Evidence of persistence of phytotoxicity is shown by dry weight yield of cucumbers as a percent of check cucumbers.

Results

Triclopyr at rate of 0.5 lb ai/A showed some inhibition of cucumber yield over period of at least 3 months, while triclopyr at rates of 3.0 and 9.0 lbs ai/A showed 50% inhibition of cucumber yield after period of at least 4 months.

Summary of Data

Rate	% of Check				
	May	June	July	Aug	Sept
0.5	22	48	50	85	124
3.0	0	20	16	48	52
9.0	0	5	6	19	47

Conclusions

Phytotoxic response of cucumbers is persistent. No analysis of soil residues of triclopyr to correlate with phytoresponse.

Hydrolysis Study

Reference D.4.0 D.4.1

"The Hydrolysis of Triclopyr in Buffered Distilled Water" by J.W. Hamaker June 5, 1975 Report GS-1410

A 3.0 ppm solution of ^{14}C-triclopyr subjected to hydrolysis at pH 5.1, 7.2 and 8.3 at 15°C, 25°C, and 35°C. Triclopyr labeled with ^{14}C in 2 and 6 position of ring. Hydrolysis conducted in buffered distilled water. Aliquots were subjected to TLC, followed by counting, to determine hydrolysis products.

Results

No significant hydrolysis of triclopyr at any pH or any temperature over 9 month interval. Several minor photodegradates, less than 1% each were identified as 3,5,6-trichloro-2-pyridinol and 2-methoxy-3,5,6-trichloropyridine. Material balance 90% or better over sampling interval. No information as to possible hydrolysis in natural waters.

Conclusions

Triclopyr is not subject to hydrolysis in buffered distilled water over long intervals.

Soil Adsorption Study

Reference D.5.0 D.5.1

"Adsorption of Triclopyr in Soil" by J. W. Hamaker Feb. 6, 1975 Report GS-1390.

Adsorption of ^{14}C-triclopyr (2,6-^{14}C) to twelve soils investigated by soil slurry method. The organic carbon content of the soils ranged from 0.081% to 21.7%. Adsorption coefficients (K_d) and (K_{oc}) were calculated. Triethylamine salt of triclopyr was used.

Results

Adsorption coefficients (K_d) ranged from 0.016 to 14.5 while K_{oc} ranged from 12 to 78. In the soil desprption study of one soil, equilibrium was reached in two days. When these results are classified as to mobility, class and K_{oc} values, triclopyr is classified as a mobile pesticide.

Photolysis Study

Reference D.6.0

"Photolysis of Triclopyr in Aqueous Solution" by J. W. Hamaker dated October 6, 1975

Triclopyr-^{14}C-2,6 subjected to photolysis in Rayonette photolyzer which closely approximates sunlight. Photolysis was at 3 pH's 5.5, 7.1, 8.1, and in "canal water."

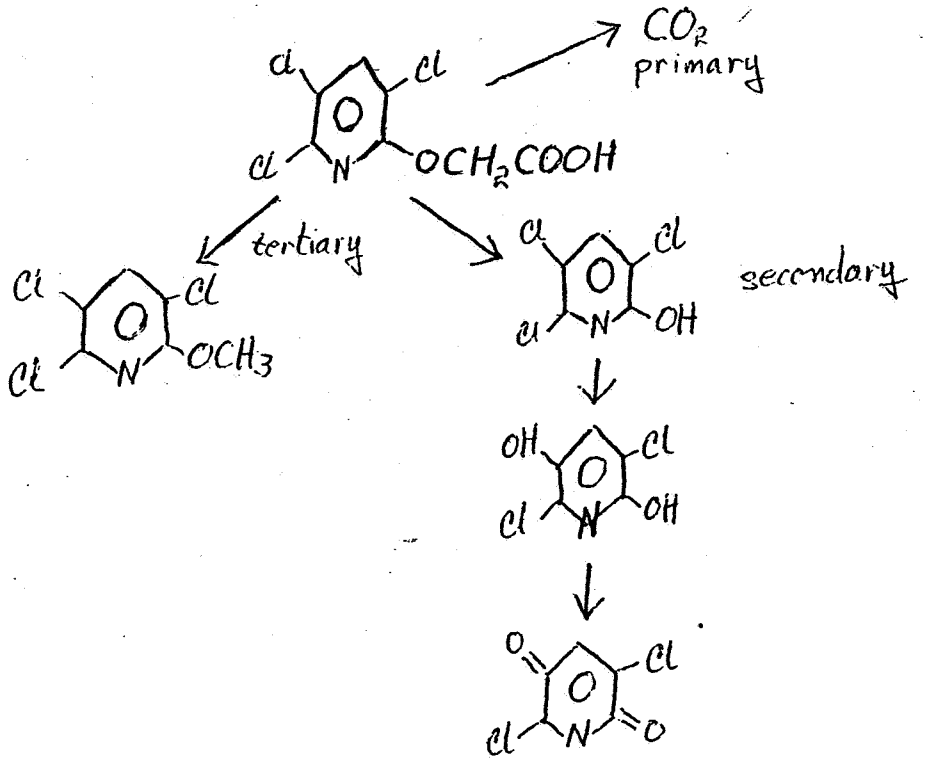
Results

Halflife of parent compound found to be less than 12 hours in all cases. Photoproducts found were trichloropyridinol (up to 10% in acidic solution but less than 3% at 7.1, 8.1 and in canal water) and possibly 2-methoxy-3,5,6-trichloropyridinol as small amounts. Polar material rapidly accrues at the origin of TLC plates, and applicant postulates that polar material at origin is polyhydroxy-pyridines or further oxidation products quinones.

Loss of ^{14}C from photolysis solution proceeds rapidly and applicant postulates that $^{14}CO_2$ is evolved. However, $^{14}CO_2$ was not accounted.

It is noted that this is a preliminary report and further report is forthcoming.

Photolysis of triclopyr



Fish Accumulation Study

Reference D.7.0 D.7.1

"Bioconcentration of Triclopyr by Catfish in a State System Containing Soil and Water" by R. W. Meikle, C. R. Youngson, A. J. Regoli dated October 1, 1975

Commerce silt loam soil (sand 26, silt 57, clay 17, organic carbon 0.76%, and pH 7.1) was treated at rate of 1.25 ppm (dry weight basis) which is 1.08 ppm at 100% of 1/3 bar moisture content. Triclopyr was radiolabeled in the 2,6-position with ^{14}C. Impurity of less than 1% was 3,5,6-trichloro-2-pyridinol-2,6-^{14}C. Treated soil was incubated in dark room at 23°C (100% relative humidity) for 30 days, after which the soil-containing aquarium was filled with 156 liters of tap water. An aliquot of soil was placed in graduate and covered with water. This soil aliquot served as submerged soil sample for assay as to soil content at the entry of fish to the aquarium after 35 days of submergence, to avoid disturbing the soil in aquarium. After 35 days of submergence (anaerobic) 35 black bullhead catfish were placed in aquarium. And after 28 days of exposure, catfish removed and placed in flowing water for depuration studies 14 days.

Time Frame

Day	Fish	Water	Soil
0-30	--	---	Aerobic
30-65	--	Exposure	Anaerobic
65-93	Exposure	Exposure	Exposure
93-104	Depuration	No exposure	--

During entire experiment, soil and aquarium water protected from light so that photodegradation would not occur. In addition, the treated soil in the aquarium was covered with aluminum screen separator to prevent stirring up the soil by catfish. The average weight of the catfish was 3.26 grams and the aquarium load was 0.73 grams of fish per liter. Standard radiometric assay procedures were used. Catfish were divided into edible portions, heads, and viscera.

Deficiencies of experiment:

1) Very similar soil in halflife study showed 1st halflife of 18 days under aerobic conditions while other soils had T/2 up to 156 days.

2) Separation of catfish from treated soil by window screen
3) Separation of submerged soil sample from aquarium soil during 35 days anaerobic submergence

Results

By the time the catfish were added to the aquarium, at day 65, only 9% of the originally applied ^{14}C was still present in the soil, and total ^{14}C in soil was only 28% of applied. Fifteen percent of applied ^{14}C was present at this sample interval in the form of 3,5,6-trichloropyridinol. It should be noted that this analysis is on soil in the separate graduate and not on the actual soil in the aquarium.

9% as parent

Parent compound triclopyr does not accumulate in edible portions of in fish heads-viscera of black bullhead catfish. The degradate 2-methoxy-3,5,6-trichlorophyridinol does not accumulate in edible or non-edible portions. The degradate 3,5,6-trichloropyridinol does not accumulate in edible portions of catfish, but does accumulate in fish heads-viscera; such accumulation, however, is not significant, since the concentration factor is about 27.

During depuration period of 12 days, the small amount of ^{14}C in edible portions gradually decreases. In fish heads-viscera, the clearing or depuration of ^{14}C compounds was not investigated.

Conclusions

Triclopyr and its two known degradates, 2-methoxy-3,5,6-trichloropyridinol and 3,5,6-trichloropyridinol do not accumulate to a significant degree in black bullhead catfish.

4.0 Conclusions

Persistence

Parent compound has low-to-moderate persistence, with halflives ranging from 10 days to 156 days. Persistence or formation of degradates not investigated. In a field study of leaching, significant phytotoxic response occurred at 3.0 and 9.0 lbs a.e./A After a minimum interval of five months, as shown by cucumber bioassay procedure.

Mobility

Parent compound and/or degradates leach readily, either as fresh residues or aged residues. Chemical nature of leaching ^{14}C was not investigated. The soil adsorption study also demonstrated mobility of parent compound, with adsorption coefficients (K_d) ranging from 0.016 to 14.5.

Hydrolysis-Photolysis

Parent compound is extremely stable to hydrolysis at pH 5.1, 7.2 and 8.3 over nine month interval.

Photolysis occurs rapidly at pH 5.5, 7.1 and 8.1 and in "canal water", with halflife of 12 hours. Transitory photoproducts were 3,5,6-trichloropyridinol and 2-methoxy-3,5,6-trichloropyridinol. Final photoproducts were unidentified polar products, possibly polyhydroxypyridines or quinones.

Accumulation

Plants - No data on accumulation in plants (no data required for this use pattern) but applicant mentions that parent compound is readily absorbed via root system or foliage and rapidly translocated.

Animals - Parent compound and its degradates do not accumulate in edible portions of black bullhead catfish. One degradate, 3,5,6-trichloropyridinol, accumulates to some degree in fish heads-viscera. Depuration of residues occur in edible portions, but depuration in fish heads-viscera was not investigated.

5.0 Recommendations

No adverse environmental chemistry comments at this time on the experimental use permit.

For registration, the following data requirements, as enumerated in our response to M-3724 application of February 25, 1974, are needed:

1. Soil persistence study under laboratory conditions of the persistence of parent and degradates through third halflife (or 12 months, whichever is shorter). Degradates should be identified and a material balance is needed. Having noted that Grazon 3 Reference No. 8.2.1 is a status report, we await the final report, assuming the final report contains the above described data. In this regard, the report GS Report 1364 "Aerobic Degradation of Ring Labeled ^{14}C-3,5,6-trichloro-2-pyridyloxyacetic acid in Soil" by A. J. Regoli and D. A. Laskowski (1974) [as reference #3 of D.4.1 and #8 of D.7.1] appears to be pertinent and should be submitted.

2. Field persistence study. (The runoff study is no longer required).

3. Tank mixture persistence data as described in our response to M-3724 submission of February 25, 1974.

4. Additionally, refer to Section 3 Regulations for registration data requirements.

5. The further report on photolysis, as described on page 2 of Reference D.6.0.

During the environmental chemistry evaluation, the following questions arose and need clarification.

In Reference D.3.1, the concentration of triclopyr and the position of the ^{14}C in the triclopyr structure need clarification.

In the field study portion of this report, the planting date is needed to determine the duration of the phytotoxic response.

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